AUSTRALIAN JOURNAL OF BASIC AND APPLIED SCIENCES

ISSN:1991-8178 EISSN: 2309-8414
Journal home page: www.ajbasweb.com

Enhancement of Heterogeneous Ethyl Oleate Synthesis Using Hydrous Ethanol

[1]M. S. Mahmud, [2]T. Safinski, [3]M. I. Nelson and [4]A. A. Adesina

[1]Faculty of Chemical & Natural Resources Engineering, Universiti Malaysia Pahang, 26300 Gambang, Pahang, Malaysia
[2]ANSTO Minerals Locked Bag 2001 Kirrawee DC NSW 2232
[3]School of Mathematics & Applied Statistics, University of Wollongong, Wollongong 2522, Australia
[4]Atodatech LLC, Los Angeles

Address For Correspondence:
Mohd Sabri Mahmud. Faculty of Chemical and Natural Resources Engineering, Universiti Malaysia Pahang, Gambang, Tun Razak Highway, 26300 Kuantan, Pahang, Malaysia. E-mail address: mohdsabri@ump.edu.my. Phone no.: +609-5492898

ARTICLE INFO

Article history:
Received 18 September 2016
Accepted 21 January 2017
Available online 26 January 2017

Keywords:
esterification, liquid-liquid extraction, immobilized lipase, fatty acid ethyl ester

ABSTRACT

Biodiesel synthesis using heterogenous catalyst usually results in compromise rate of reaction due to mass transfer limitation during the reaction. An alternative is reported in this paper to produce biodiesel from free fatty acids in a liquid-liquid system using immobilized lipase. The yield of reversible reactions, which is naturally deteriorated by the presence of water because of thermodynamic limitation, nevertheless remained and the rate increased until 2 manifolds when water was initially added from 0.15 wt% to 15 wt%. The reaction tests were conducted in a batch reactor at 45ºC using the feed ratio, β ($0 < \beta < 2.5$) and all runs were performed under free mass transport limitation. The result also shows that the increment of rates were prominent in excess oleic acid mixtures implying the enhancement of clearly discriminated liquid phase during the reaction.

INTRODUCTION

Biodiesel is a renewable source of energy that is derived from plants and animals. Most feedstock of the biodiesel production comes from waste cooking oils and non-edible oils. Free fatty acids (FFAs) are particularly side products of oleo chemical industries (Echim *et al*., 2009) and have the potential to become the biodiesel feedstock as well through esterification reaction. The process using FFA however requires acidic conditions or enzymes which are not merely promising due to slow reaction or high capital cost.

Immobilized lipase is an alternative to solve the recovery issue of expensive enzyme. It becomes more interesting when it showed enhancement in esterification reactions with traces of water initially added (Foresti *et al*., 2008). Active site of lipase is naturally hydrophilic but the support that is normally made of polymer resin will float the biocatalyst in organic media due to its density and will be directly involved with the main reaction. The reaction normally starts with attachment of FFA molecules onto the active site of lipase and will result in their conformational change to intermediate molecules. Mixing that creates turbulent regime ensures effective contact between FFA and dissolved alcohol. Ester will be produced as a polar organic molecule.

An unreacted alcohol and esters can form aqueous phase along with water in the esterification of FFA. Diffusion of esters from active site to the second phase will drive the reversible reaction of FFA esterification towards products. Chemical species that emerge or diminish during the esterification reaction will then have different solubility and creates different conditions of liquid phase in substrate depending on the initial reactant ratio.

Ethanol is the second favorite alcohol in biodiesel synthesis studies due to its renewable resources and advantageous fuel property compared to methanol. However, its miscibility with FFA is high. Addition of water

To Cite This Article: M. S. Mahmud, T. Safinski, M. I. Nelson and A. A. Adesina., Enhancement of Heterogeneous Ethyl Oleate Synthesis Using Hydrous Ethanol. ***Aust. J. Basic & Appl. Sci.,*** *11(3): 160-164, 2017*

can create the second phase besides reducing toxicity of the alcohol on lipase. The aim of this study is therefore to evaluate the effect of water at high content than proposed by Foresti *et al*. (2008) on the esterification reaction using immobilized lipase. Oleic acid (OA) was used as it is the dominant fatty acid in many vegetable oils.

MATERIALS AND METHODS

Novozym 435, a commercial immobilized lipase (*Aspergillus niger*) on macroporous acrylic resin (383 µm particles) was obtained from Novozyme Pty. Ltd. 95% pure oleic acid used for reaction and high performance liquid chromatography (HPLC)-grade methanol (99.5%) used for analysis sample preparation were supplied by Ajax Fine Chemicals (Sydney, Australia) and absolute ethanol was provided by APS Chemicals (Sydney, Australia). Sigma Aldrich provided the analytical oleic acid (98%) and ethyl oleate (98%) for the gas chromatography (GC) calibration.

All reaction runs were carried out in a 500 mL cylindrical Pyrex glass vessel at 45°C. 1 wt% fresh catalyst was used for each run. 20 µL aliquots were taken at appropriate time intervals to determine component transients using GC. Detail description of rig setup, experimentation for reactions and analytical equipment procedures were reported in our previous paper (Mahmud, Safinski, Nelson, Sidhu, & Adesina, 2009).

Experiments to study the effect of water content were conducted similarly. The water content was prepared by adding initially ultrapure Mill-Q water for 0.15%, 2.5% and 15% water on the weight basis to make up the reactor volume. The molar feed ratio was tested spanning from 0.4 to 2.5. Fig. 1 shows the location of substrate, lipase and water in the reactor glass as the experiment finished and the stirrer stopped.

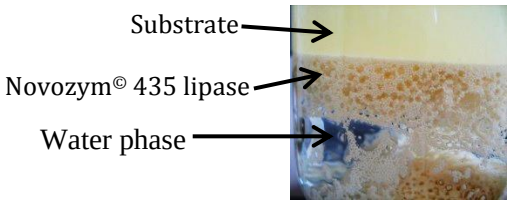

Fig. 1: Reactor content image after reaction

RESULTS AND DISCUSSION

Esterification reaction of oleic acid with ethanol is reversible but low solubility of by-product water in the organic media led the limiting reactant to convert considerably high at equilibrium conditions. Fig. 2 (a) and (b) exhibit the exemplary conversion profiles of limiting reactant, *X*, for three feed ratios adequately representing two groups of test. The same trend was followed by other ratios and groups which are not shown here for the sake of simplicity. The model of exponential rise to equilibrium conversion well fits the result data with R^2 not lower than 98% which is generally expressed as in Eq. (1) and shown by the trend line in Fig. 2.

$$X = X_{eq}[1 - \exp(-bt)] \quad (1)$$

X_{eq} is the final conversion of limiting reactant at equilibrium and *b* is frequency of reaction.

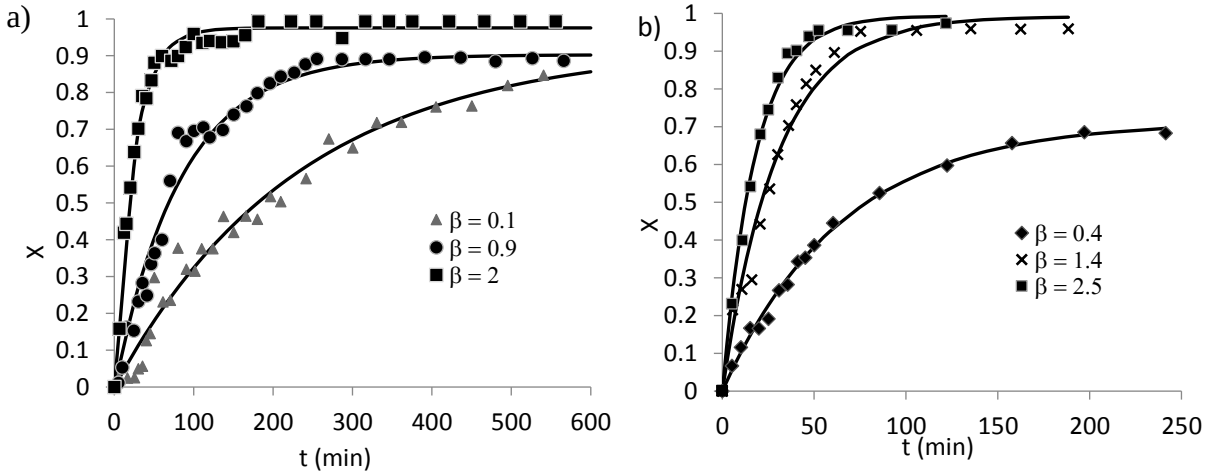

Fig. 2: Conversion profiles against reaction time for various OA:Ethanol feed ratios, β with (a) no water and (b) 2.5 wt% water initially added, respectively

In our previous study (Mahmud *et al*., 2009), the time to determine initial rate was after 40 min where the internal transport resistance for the catalyst is negligible. The feed ratio of the reaction test was 1:1 without any additional water and the conversion was 54%. From the conversion profile in Fig. 2, the time for all the reaction tests to reach equilibrium is clearly not same for all as the result of dissimilar feed ratio and presence of water. The equilibria probably reached when both forward and reverse reactions, which stopped at a certain ratio of component concentrations, the equilibrium constant, progressed at different rates in accordance with Eq. (2) (Fogler, 2005)

$$K_{eq} = \frac{r_{foward}}{r_{reverse}} = \frac{Fn\,(T,C_i)}{Fn\,(T,C_j)} \quad (2)$$

Where Fn is function, r is reaction rate, T is reaction absolute temperature, i subscript is reactant and j subscript is product.

The rate of reaction is expressed according to the mole balance of the batch reactor as Eq. (3)

$$-r_A = C_{A0}\frac{dX}{dt} = C_{A0}X_{eq}b\exp(-bt) \quad (3)$$

where the C_{A0}, X_{eq} and b are the intensity term and parameter (ITP) that will result in high reaction rate if they are high. Their values with respect to initial water contents are summarized in

Table **1**.

Table 1: Summary of reaction parameters

Water	β	C_{A0}	X_{eq}	b
No water initially added	0.01	0.162	9214.571	9.95×10^{-8}
	0.05	0.666	0.959	0.0042
	0.1	1.091	0.927	0.0043
	0.25	1.766	0.934	0.0052
	0.5	2.224	0.885	0.0097
	0.63	2.346	0.945	0.0093
	0.75	2.435	0.903	0.0118
	1	2.557	0.912	0.0117
	1.2	2.185	0.950	0.027
	1.4	1.907	0.967	0.027
	1.6	1.693	0.966	0.0385
	2	1.381	0.976	0.0412
0.15 wt%	0.4	2.087	1	4.8×10^{-3}
	0.65	2.364	1	0.0103
	0.9	2.512	1	0.0166
	1.15	2.267	1	0.0304
	1.4	1.907	0.993	0.0502
	1.7	1.602	1	0.0473
	2	1.381	1	0.0645
	2.5	1.123	0.999	0.1063
2.5 wt%	0.4	2.058	0.714	0.0153
	0.65	2.327	0.85	0.0155
	0.9	2.471	0.796	0.0221
	1.15	2.267	1	0.0253
	1.4	1.907	0.992	0.0331
	1.7	1.602	0.978	0.0438
	2.5	1.123	0.994	0.0551
15 wt%	0.4	1.919	0.9	0.008
	0.65	2.151	0.844	0.0166
	0.9	2.273	0.767	0.0228
	1.4	1.907	0.961	0.0281
	2	1.381	0.976	0.0487

ITP is used to indicate the reaction rate. Fig. 3 shows increment of ITP against the OA:ethanol feed ratios for various water additions. All tests exhibit low ITP values below the stoichiometric ratio of unity. Nevertheless, the tests with initial water addition improved it double and 1.5 time in 2.5 wt% water and other tests having initial water addition, respectively. On the other hand, all tests exhibit relatively high values above the stoichiometric ratio. The tests with water content are higher than the one without initial water addition and are dominated by 0.15 wt% test which shows 1.5 time higher. The 15 wt% test shows declination of ITP values close to reference of the test without initial water addition.

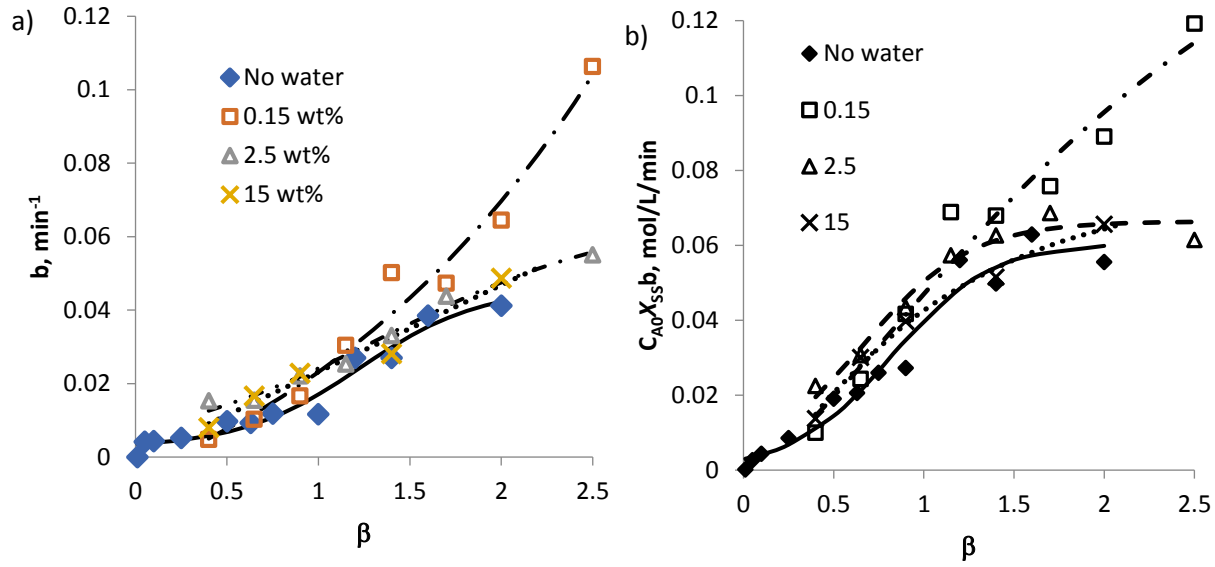

Fig. 3: The (a) frequency of reaction, *b* and (b) intensity term versus feed ratio for various water compositions

If this result is compared to previously similar works, the study on the same reaction using the same reactant is probably the right benchmark. To the best of author's knowledge, no paper reported exactly the same reaction setup. Foresti *et al.* (2008) used Candida's lipase that they immobilized onto chitosan to investigate the effect of 0 wt% and 9.6 wt% water using the stoichiometric mixture of oleic acid and ethanol. The result conforms to our result on the same reactant ratio although the commercial Novozym 435 was used.

The tests with access ethanol shows low reaction rate elements of ITP probably due to its toxicity to lipase. The addition of water especially at the content greater than 1 wt% reduced this effect as it created a second phase of aqueous ethanol (Goncalves, Batista, & Meirelles, 2002) reducing dissolved ethanol in the organic phase where most lipase was present.

As oleic acid became excess, $\beta > 1$, more lipase will have chance to initiate carboxylic group break-up which is the limiting step of the free fatty acid esterification reaction and thus high ITP. The addition of traces of water (0.15 wt%) enhanced the activity of lipase active site (M.L. Foresti, Pedernera, Bucala, & Ferreira, 2007; Mahmud *et al*., 2009). More water initially added to the substrate (2.5 wt% to 15 wt%) had lowered this enhancement suggesting that the thermodynamic limitation began to appear.

Conclusion Remarks:

Water addition to the oleic acid-ethanol esterification reaction generally improved the reaction rate. The tests were conducted at 45°C under conditions of free mass transfer limitation. Traces of water, 0.15wt%, amplified the activity of the immobilized lipase at the highest level. Adding more water created a second phase of aqueous ethanol and surprisingly improved the reaction rate as well. This study found the greater enhancement of excess oleic acid for the esterification reaction of free fatty acid and ethanol using immobilized lipase.

ACKNOWLEDGEMENT

The author wishes to thank the Ministry of Science, Technology and Innovation (MOSTI), Malaysia for the National Science Fellowship awarded to MSM and for the IRPA 02-02-02-0004-PR0023/11-09 grant awarded to Prof. Ir. Dr. Zahira Yaakob and Prof. Ir. Dato' Dr. Wan Ramli Wan Daud.

REFERENCES

Echim, C., R. Verhe, W. De Greyt and C. Stevens, 2009. Production of biodiesel from side-stream refining products. [10.1039/B905925C]. Energy & Environmental Science, 2(11): 1131-1141. doi: 10.1039/b905925c

Fogler, H.S., 2005. *Elements of Chemical Reaction Engineering* (3 ed.). New Jersey: Prentice-Hall International Inc.

Foresti, M.L., M. Pedernera, V. Bucala and M.L. Ferreira, 2007. Multiple effects of water on solvent-free enzymatic esterifications. Enzyme and Microbial Technology, 41: 62-70.

Foresti, M.L., M. Pedernera, M.L. Ferreira and V. Bucala, 2008. Kinetic modeling of enzymatic ethyl oleate synthesis carried out in biphasic systems. Applied Catalysis A: General, 334(1-2): 65-72.

Goncalves, C.B., E. Batista and A.J.A. Meirelles, 2002. Liquid-liquid equilibrium data for the system corn oil + oleic acid + ethanol + water at 298.15 K. Journal of Chemical & Engineering Data, 47(3): 416-420. doi: doi:10.1021/je010273p

Mahmud, M.S., T. Safinski, M.I. Nelson, H.S. Sidhu and A.A. Adesina, 2009. Kinetic Analysis of Oleic Acid Esterification Using Lipase as Catalyst in a Microaqueous Environment. Industrial & Engineering Chemistry Research, 49(3): 1071-1078.